

Chinese Patent No. 1371924A

Job No.: 6194-94961

Translated from Chinese by the Ralph McElroy Translation Company
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INTELLECTUAL PROPERTY OFFICE OF THE
PEOPLE'S REPUBLIC OF CHINA
PUBLIC DESCRIPTION OF INVENTION
PATENT APPLICATION
PATENT NO. 1371924A

Int. Cl. ⁷ :	C 08 F 10/02 C 08 F 4/70
Filing Date:	March 4, 2002
Filing No.:	02104276.4
Publication Date:	October 2, 2002
No. of pages of the claims:	4 pages of
No. of pages of the description:	13 pages
No. of pages of figures:	0 pages

POLYMERIZED NICKEL-ZIRCONIUM DOUBLE ACTIVE SITE OLEFIN
POLYMERIZATION CATALYST

Inventors:	Jin Guoxin Zhang Dao Li Xiaoming
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Applicant:	Chinese Academy of Science Changchun Applied Chemistry Research Institute Post No. 159 Renmind Street, Changchun City, Jilin Province 130022
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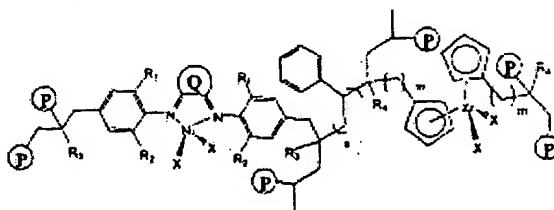
Abstract

The present invention relates to the preparation of a polymerized double active site olefin polymerization catalyst and catalytic olefin polymerization. The catalyst is composed of Component A and Component B. The formula for Component A is $[P(\text{ComNi-co-S-co-ComZr})]$

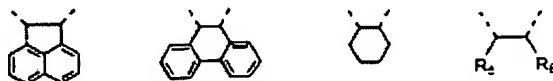
or $[\text{SiO}_2\text{-P(ComNi-co-S-co-ComZr)}]$ where P represents a copolymer, S represents styrene, co represents copolymerization, ComNi represents an alkenyl group-containing "post-metallocene" α -diimide nickel-based catalyst, and ComZr represents an alkenyl group-containing metallocene zirconium catalyst. $[\text{P(ComNi-co-S-co-ComZr)}]$ is a copolymer of α -diimide nickel catalyst, a metallocene catalyst and styrene. SiO_2 represents silicon dioxide as the support. Component B is any of methylaluminoxane (MAO), modified methylaluminoxane (MMAO) and pentafluorophenylborane $[\text{B}(\text{C}_6\text{F}_5)_3]$. This type of catalyst has a relatively high activity in the catalysis of ethylene polymerization. It is appropriate in gas-phase and slurry polymerization processes. The polymer does not contain inorganic ash.

Claims

1. A polymerized nickel-zirconium double active site olefin polymerization catalyst is composed of Component A and Component B, characterized by the fact that the formula for Component A is $[\text{P(ComNi-co-S-co-ComZr)}]$ or $[\text{SiO}_2\text{-P(ComNi-co-S-co-ComZr)}]$, where P represents a copolymer, S represents polystyrene, co represents copolymerization, ComNi represents an alkenyl group-containing "post-metallocene" α -diimide nickel-based catalyst, and ComZr represents an alkenyl group-containing metallocene zirconium catalyst, $[\text{P(ComNi-co-S-co-ComZr)}]$ is a copolymer of α -diimide nickel catalyst, a metallocene catalyst and styrene and has the following structural formula:



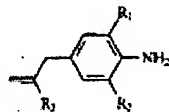
in this formula, m is an integer of 0-4; n is an integer of 0-100; X is Cl or Br; R_1 and R_2 can be the same or different and may be hydrogen, methyl groups, isopropyl groups or tert-butyl groups; R_3 is any of hydrogen, a methyl group, an isopropyl group or a butyl group; and R_3 [sic; R_4] is hydrogen or a methyl group; Q is selected from the following divalent residues of cyclic compounds or their mixture:



in this formula, R_5 and R_6 can be the same or different and may be methyl groups, ethyl groups, propyl groups or heterocycles; SiO_2 represents the silicon dioxide support. Component B is any of methylaluminoxane (MAO), modified methylaluminoxane (MMAO) and pentafluorophenyl borane $[\text{B}(\text{C}_6\text{F}_5)_3]$.

2. A method for the preparation of Component A of the polymerized nickel-zirconium double active site olefin polymerization catalyst described in Claim 1, including:

an N-alkenylaniline formed from an aromatic amine and an alkenyl chloride or an alkenyl bromide is rearranged in the presence of anhydrous zinc chloride to obtain 4-alkenyl aromatic amine at a yield of 25-71%:

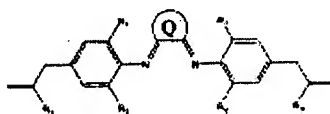


in this formula, R_1 and R_2 can be the same or different and may be H, methyl groups, isopropyl groups or tert-butyl groups; R_3 is H, a methyl group, an ethyl group, a propyl group or a butyl group;

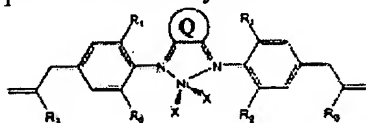
it undergoes a condensation reaction with an α -diketone shown by the following formula under the catalysis of formic acid, acetic acid, trifluoroacetic acid or hydrochloric acid in an acid and alcohol solvent:



to obtain an alkenyl group-containing α -diimide ligand shown by the following formula at a yield of 72-84%;



under water-free and oxygen-free conditions, the ligand mentioned previously is subjected to a coordination reaction with NiX_2 , in which X is Cl or Br, to obtain an alkenyl group-containing α -diimide Ni(II) coordination compound shown by the following formula at a yield of 92-98%;

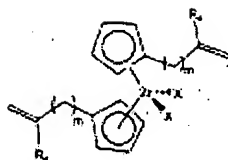


by using tetrabutylammonium bromide as a phase transition agent, cyclopentadiene and a halogen-substituted olefin are reacted to obtain the following alkenylcyclopentadiene at a yield of 40-70%;



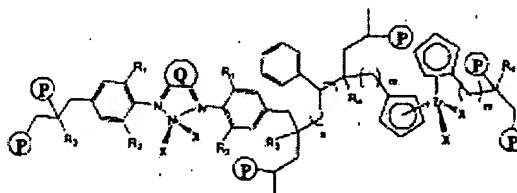
in this formula, m is an integer of 0-4, and R_4 is hydrogen or a methyl group;

in a tetrahydrofuran system, the alkenylcyclopentadiene mentioned previously is treated with equimolar n-BuLi and reacted with $ZrCl_4$ at an equivalent amount to obtain the following alkenyl metallocene catalyst at a yield of 60-75%;



in this formula, X is Cl or Br; m is an integer of 0-4; R_4 is hydrogen or a methyl group;

under water-free and oxygen-free conditions, the alkenyl group-containing α -diimide Ni(II) coordination compound and the alkenyl group-containing metallocene catalyst are copolymerized with styrene under the initiation of AIBN (AIBN being azobisisobutyronitrile) to cause the catalyst to link with polyethylene [sic; polymer] chains through σ bonds to obtain the polymerized double active site olefin polymerization catalyst of the following formula:



in this formula, m is an integer of 0-4; n is an integer of 0-100; X is Cl or Br; R_1 and R_2 can be the same or different and may be hydrogen, methyl groups, isopropyl groups or tert-butyl groups; R_3 is any of hydrogen, a methyl group, an isopropyl group or a butyl group; and R_4 [sic; R_3] is hydrogen or a methyl group; Q is selected from the following divalent residues of cyclic compounds or their mixture:



in this formula, R_5 and R_6 can be the same or different and may be methyl groups, ethyl groups, propyl groups or heterocycles; SiO_2 represents the silicon dioxide support for supporting the polymerized catalyst [P(ComNi-co-S-co-ComZr)];

under the action of the promoter Component B (Component B being methylaluminoxane (MAO), modified methylaluminoxane (MMAO) or pentafluorophenyl borane [$B(C_6F_5)_3$]), Component A catalyzes the olefin polymerization at 1-20 atm and the activity is 10^5 - 10^7 g PE (mol Ni·h)⁻¹.

3. A method for the preparation of the polymerized nickel-zirconium double active site olefin polymerization catalyst described in Claims 1 and 2, characterized by the fact that, during the process of preparation of Component A of the polymerized α -diimide nickel-based catalyst carried on silicon dioxide, the silicon dioxide support, the solvent and the catalyst are added first, heated to a temperature of $70 \pm 0.5^\circ\text{C}$, the initiator is then added, and polymerization is conducted by maintaining the temperature at $80 \pm 0.5^\circ\text{C}$ for 8 h.

4. A method for the preparation of the polymerized "post-metallocene" α -diimide nickel-based olefin polymerization catalyst described in Claim 1, characterized by the fact that, in the process for the production of polyethylene, the step of using Component A of the polymerized nickel-zirconium double active site olefin polymerization catalyst described in Claim 1 is included.

5. A method for the preparation of the polymerized nickel-zirconium double active site olefin polymerization catalyst described in Claim 1, characterized by the fact that the polymerization pressure in the production of polyethylene is 1-20 atm.

6. A method for the preparation of the polymerized nickel-zirconium double active site olefin polymerization catalyst described in Claim 1, characterized by the fact that homogeneous polymerization and heterogeneous polymerization are adopted in the production of polyethylene.

Description

Technical field

The present invention relates to an olefin polymerization catalyst. More specifically, it relates to a polymerized olefin polymerization catalyst containing nickel and zirconium double active sites.

The present invention also relates to a method for the preparation of the catalyst mentioned previously.

The present invention also relates to the application of the catalyst mentioned previously to olefin polymerization, especially to ethylene polymerization.

Background of the technology

The third-generation, high-activity olefin polymerization catalysts as the "post-metallocene" late transition metal catalysts initiated at the end of the last century and honored in the same way as the Ziegler-Natta catalyst and the metallocene catalyst have now become the hottest research topic in new olefin polymerization catalysts in the whole world. However, the traditional early transition metal catalyst is still exhibiting a huge effect in modern industrial production. How to combine the excellent characteristics of the early transition metal catalyst and the late transition metal catalyst in order to prepare a polyolefin material with novel structure and performance has now become an important research direction for olefin polymerization. Chinese patents (Nos. 98125651.1, 1998 and 01140470.1, 2001) disclose respectively the method for the preparation of the polymerized metallocene olefin polymerization catalyst and the method for the preparation of the polymerized late transition metal "post-metallocene" nickel-based olefin polymerization catalyst. The polymerized nickel-zirconium double active site catalyst has not been reported. This work has significance regarding the aspects of obtaining a

polymer with ideal molecular weight and degree of branching, adapting to a commercialized production apparatus, increasing the physical processing performance of the polymer, etc.

Content of the invention

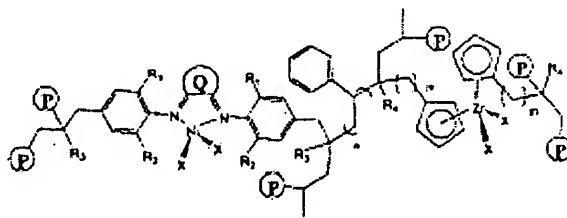
One objective of the present invention is to provide a polymerized nickel-zirconium double active site olefin polymerization catalyst.

Another objective of the present invention is to provide a method for the preparation of a polymerized nickel-zirconium double active site olefin polymerization catalyst. In said method, a group IVB metallocene compound containing an olefin substitute group and an α -diimide nickel-based catalyst are used in the polymerization with styrene under the action of an initiator so that the pre- and late-transition metal catalysts are connected through σ bonds to the polymer chain to form a polymerized nickel-zirconium double active site olefin polymerization catalyst.

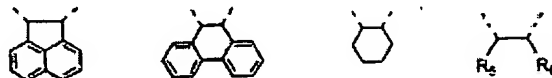
The third objective of the present invention is to provide the polymerized nickel-zirconium double active site catalyst for application in olefin polymerization, especially ethylene polymerization.

The polymerized nickel-zirconium double active site catalyst has a very high catalytic activity for olefin polymerization in the same manner. Furthermore, by the polymerization of pre- and late-transition metal catalysts, the composition and the distribution of the catalyst on the polymer chains can be controlled very easily. By adjusting the distribution of the catalyst on the polymer chains, the catalytic effect of the active sites can be enhanced to the utmost extent and improvements in physical, mechanical and processing performance of the polymers can be achieved. In addition, the polymers obtained by the olefin polymerization catalyzed by the polymerized nickel-zirconium double active sites do not contain inorganic ash.

The catalyst prepared according to the present invention is composed of Component A and Component B, in which the formula for Component A is $[P(\text{ComNi-co-S-co-ComZr})]$ or $[\text{SiO}_2\text{-P}(\text{ComNi-co-S-co-ComZr})]$, where P represents a copolymer, S represents polystyrene, co represents copolymerization, ComNi represents an alkenyl group-containing "post-metallocene" α -diimide nickel-based catalyst, and ComZr represents an alkenyl group-containing metallocene zirconium catalyst. $[P(\text{ComNi-co-S-co-ComZr})]$ is a copolymer of α -diimide nickel catalyst, a metallocene catalyst and styrene and has the following structural formula:



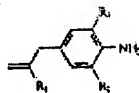
In this formula, m is an integer of 0-4; n is an integer of 0-100; X is Cl or Br; R_1 and R_2 can be the same or different and may be hydrogen, methyl groups, isopropyl groups or tert-butyl groups; R_3 is any of hydrogen, a methyl group, an isopropyl group or a butyl group; and R_4 is hydrogen or a methyl group; Q is selected from the following divalent residues of cyclic compounds or their mixture:



In this formula, R_5 and R_6 can be the same or different and may be methyl groups, ethyl groups, propyl groups or heterocycles; SiO_2 represents the silicon dioxide support for carrying the polymerized catalyst $[P(ComNi-co-S-co-ComZr)]$. Component B is any of methylaluminoxane (MAO), modified methylaluminoxane (MMAO) and pentafluorophenylborane $[B(C_6F_5)_3]$.

The preparation process for the catalyst is shown in the following:

An N-alkenylaniline formed from an aromatic amine and an alkenyl chloride or an alkenyl bromide is rearranged in the presence of anhydrous zinc chloride to obtain a 4-alkenyl aromatic amine at a yield of 25-71%:

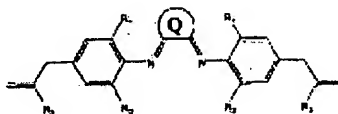


In this formula, R_1 and R_2 can be the same or different and may be H, methyl groups, isopropyl groups or tert-butyl groups; R_3 is H, a methyl group, an ethyl group, a propyl group or a butyl group:

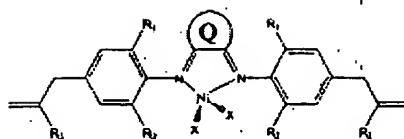
It undergoes a condensation reaction with an α -diketone shown by the following formula under the catalysis of formic acid, acetic acid, trifluoroacetic acid or hydrochloric acid in an acid and alcohol solvent:



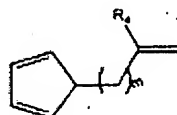
to obtain an alkenyl group-containing α -diimide ligand shown by the following formula at a yield of 72-84%;



Under water-free and oxygen-free conditions, the ligand mentioned previously is subjected to a coordination reaction with NiX_2 , in which X is Cl or Br, to obtain an alkenyl group-containing α -diimide Ni(II) coordination compound shown by the following formula at a yield of 92-98%:

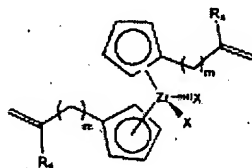


By using tetrabutylammonium bromide as a phase transition agent, cyclopentadiene and a halogen-substituted olefin are reacted to obtain the following alkenylcyclopentadiene at a yield of 40-70%:



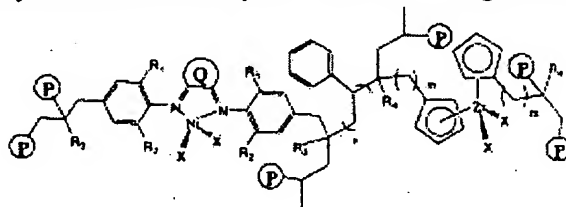
In this formula, m is an integer of 0-4, and R_4 is hydrogen or a methyl group:

In a tetrahydrofuran system, the alkenylcyclopentadiene mentioned previously is treated with equimolar $n\text{-BuLi}$ and reacted with ZrCl_4 at an equivalent amount to obtain the following alkenyl metallocene catalyst at a yield of 60-75%:

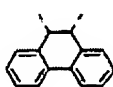


In this formula, X is Cl or Br ; m is an integer of 0-4; R_4 is hydrogen or a methyl group.

Under water-free and oxygen-free conditions, the alkenyl group-containing α -diimide Ni(II) coordination compound and the alkenyl group-containing metallocene catalyst are copolymerized with styrene under the initiation of AIBN (AIBN being azobisisobutyronitrile) to cause the catalyst to link with polyethylene chains through σ bonds to obtain the polymerized double active site olefin polymerization catalyst of the following formula:



In this formula, m is an integer of 0-4; n is an integer of 0-100; X is Cl or Br ; R_1 and R_2 can be the same or different and may be hydrogen, methyl groups, isopropyl groups or tert-butyl groups; R_3 is any of hydrogen, a methyl group, an isopropyl group or a butyl group; and R_4 is hydrogen or a methyl group; Q is selected from the following divalent residues of cyclic compounds or their mixture:



In this formula, R_5 and R_6 can be the same or different and may be methyl groups, ethyl groups, propyl groups or heterocycles; SiO_2 represents the silicon dioxide support for carrying the polymerized catalyst $[P(ComNi-co-S-co-ComZr)]$:

Under the action of the promoter Component B (Component B being methylaluminoxane (MAO), modified methylaluminoxane (MMAO) or pentafluorophenyl borane $[B(C_6F_5)_3]$), Component A catalyzes the olefin polymerization at 1-20 atm and the activity is 10^5 - 10^7 g PE $(mol\ Ni \cdot h)^{-1}$.

Specific application embodiments are as follows:

Application Example 1: Preparation of an allyl type aromatic amine

2, 6-Diisopropylaniline 0.2 mol and allyl chloride 0.1 mol were refluxed by heating for 8 h, cooled by standing overnight, poured into 400 mL of water, made alkaline by using a sodium hydroxide solution, extracted with ethyl ether, and distilled under reduced pressure to obtain 18.33 g of N-allyl-2,6-diisopropylaniline at a yield of 84%. Toluene as a solvent was added at 100 mL into 0.084 mol of the N-allyl-2,6-diisopropylaniline and 0.1 mol of anhydrous zinc chloride. It was refluxed under an argon gas atmosphere for 5 h. It was cooled and poured into a sodium hydroxide aqueous solution to make it alkaline. The organic phase was removed. The bottom layer of insoluble material was dissolved in hot concentrated hydrochloric acid. It was poured into the ethyl ether extract solution mentioned previously, dried over anhydrous magnesium sulfate, concentrated under vacuum, and then distilled under reduced pressure to obtain 12.92 g of 4-allyl-2,6-diisopropylaniline at a yield of 71%.

Application Example 2: Preparation of an allyl type aromatic amine

2-Tert-butylaniline 0.1 mol and 1-bromo-2-butene 0.05 mol were refluxed by heating for 10 h, cooled by standing overnight, poured into 200 mL of water, made alkaline by using a sodium hydroxide solution, extracted with ethyl ether, and distilled under reduced pressure to obtain 5.35 g of N-(2-methylpropenyl)-2-tert-butylaniline at a yield of 53%. Toluene as a solvent was added at 200 mL into 0.2 mol of the N-(2-methylpropenyl)-2-tert-butylaniline and 0.2 mol of anhydrous zinc chloride. It was refluxed under an argon gas atmosphere for 8 h. It was cooled and poured into a sodium hydroxide aqueous solution to make it alkaline. The organic phase was removed. The bottom layer of insoluble material was dissolved in hot concentrated hydrochloric acid. It was poured into the ethyl ether extract solution mentioned previously, dried over anhydrous magnesium sulfate, concentrated under vacuum, and then distilled under reduced pressure to obtain 24.89 g of 4-(2-methylpropenyl)-2-tert-butylaniline at a yield of 61%.

Application Example 3: Preparation of an allyl type aromatic amine

2, 6-Dimethylaniline 0.12 mol and 1-bromo-2-pentene 0.06 mol were refluxed by heating for 9 h, cooled by standing overnight, poured into 300 mL of water, made alkaline by using a sodium hydroxide solution, extracted with ethyl ether, and distilled under reduced pressure to obtain 3.72 g of N-(2-ethylpropenyl)-2,6-dimethylaniline at a yield of 33%. Toluene as a solvent was added at 80 mL into 0.05 mol of the N-(2-ethylpropenyl)-2,6-dimethylaniline and 0.05 mol of anhydrous zinc chloride. It was refluxed under an argon gas atmosphere for 7 h. It was cooled and poured into a sodium hydroxide aqueous solution to make it alkaline. The organic phase was removed. The bottom layer of insoluble material was dissolved in hot concentrated hydrochloric acid. It was poured into the ethyl ether extract solution mentioned previously, dried over anhydrous magnesium sulfate, concentrated under vacuum, and then distilled under reduced pressure to obtain 2.77 g of 4-allyl-2,6-dimethylaniline at a yield of 29%.

Application Example 4: Preparation of an allyl type aromatic amine

2, 6-Diisopropylaniline 0.1 mol and 1-bromo-2-heptene 0.05 mol were refluxed by heating for 10 h, cooled by standing overnight, poured into 300 mL of water, made alkaline by using a sodium hydroxide solution, extracted with ethyl ether, and distilled under reduced pressure to obtain 4.09 g of N-(2-butylpropenyl)-2,6-diisopropylaniline at a yield of 30%. Toluene as a solvent was added at 50 mL into 0.05 mol of the N-(2-butylpropenyl)-2,6-diisopropylaniline and 0.05 mol of anhydrous zinc chloride. It was refluxed under an argon gas atmosphere for 8 h. It was cooled and poured into a sodium hydroxide aqueous solution to make it alkaline. The organic phase was removed. The bottom layer of insoluble material was dissolved in hot concentrated hydrochloric acid. It was poured into the ethyl ether extract solution mentioned previously, dried over anhydrous magnesium sulfate, concentrated under vacuum, and then distilled under reduced pressure to obtain 3.44 g of 4-(2-butylallyl)-2,6-diisopropylaniline at a yield of 25%.

Application Example 5: Preparation of a diimide bidentate coordination compound containing two alkenyl groups

2 mmol of α -acenaphthenone and 4 mmol of 4-allyl-2,6-diisopropylaniline were dissolved in 20 mL of acetic acid, refluxed by heating for 1 h, and cooled to room temperature to obtain a solid precipitate. This was filtered, washed with acetic acid (3 x 20 mL), washed with normal hexane (3 x 20 mL), and dried under vacuum to obtain 1.0 g of an α -diimide coordination compound $C_{42}H_{48}N_2$ at a yield of 84%.

Application Example 6: Preparation of a diimide bidentate coordination compound containing two alkenyl groups

3 mmol of α -succine ketone [sic] and 6 mmol of 4-(2-methylallyl)-2-tert-butyraniline were dissolved in 30 mL of methanol, and 3-5 drops of formic acid were added as a catalyst. It was refluxed by heating for 1 h and cooled to room temperature to obtain a solid precipitate. This was filtered, washed with methanol (3 x 20 mL), washed with normal hexane (3 x 20 mL), and dried under vacuum to obtain 1.2 g of an α -diimide coordination compound $C_{36}H_{52}N_2$ at a yield of 80%.

Application Example 7: Preparation of a diimide bidentate coordination compound containing two alkenyl groups

2.5 mmol of α -cyclohexanedione and 5 mmol of 4-allyl-2,6-dimethylaniline were dissolved in 25 mL of ethanol, and 3-5 drops of hydrochloric acid were added as a catalyst. It was refluxed by heating for 1 h and cooled to room temperature to obtain a solid precipitate. This was filtered, washed with ethanol (3 x 20 mL), washed with normal hexane (3 x 20 mL), and dried under vacuum to obtain 1.0 g of an α -diimide coordination compound $C_{28}H_{34}N_2$ at a yield of 72%.

Application Example 8: Preparation of a diimide bidentate coordination compound containing two alkenyl groups

2.5 mmol of α -phenanthrenedione and 5 mmol of 4-(2-butylallyl)-2,6-diisopropylaniline were dissolved in 30 mL of methanol, refluxed by heating for 1 h, and cooled to room temperature to obtain a solid precipitate. This was filtered, washed with methanol (3 x 20 mL), washed with normal hexane (3 x 20 mL), and dried under vacuum to obtain 1.5 g of an α -diimide coordination compound $C_{52}H_{66}N_2$ at a yield of 82%.

Application Example 9: Preparation of an α -diimide nickel-based catalyst containing two alkenyl groups

The preparation of the catalyst was conducted under oxygen-free, water-free conditions with protection of high-purity argon. With 30 mL of dichloromethane as a solvent, 1 mmol of the diimide coordination compound obtained in Application Example 5 and 1 mmol of $[Ni(DME)Br_2]$ (where DME is dimethyl diethyl ether) were stirred at room temperature for 12 h, and the solvent was removed by vacuum concentration. The precipitate was washed with 50 mL of ethyl ether 3-5 times and dried under vacuum to obtain 0.8 g of an α -diimide nickel-based catalyst $C_{42}H_{48}N_2NiBr_2$ at a yield of 98%.

Application Example 10: Preparation of an α -diimide nickel-based catalyst containing two alkenyl groups

The preparation of the catalyst was conducted under oxygen-free, water-free conditions with protection of high-purity argon. With 40 mL of dichloromethane as a solvent, 1 mmol of the diimide coordination compound obtained in Application Example 6 and 1 mmol of $[\text{Ni}(\text{DME})\text{Cl}_2]$ (where DME is dimethyl diethyl ether) were stirred at room temperature for 48 h, and the solvent was removed by vacuum concentration. The precipitate was washed with 50 mL of ethyl ether 3-5 times and dried under vacuum to obtain 0.6 g of an α -diimide nickel-based catalyst $\text{C}_{36}\text{H}_{52}\text{N}_2\text{NiCl}_2$ at a yield of 98%.

Application Example 11: Preparation of an α -diimide nickel-based catalyst containing two alkenyl groups

The preparation of the catalyst was conducted under oxygen-free, water-free conditions with protection of high-purity argon. With 30 mL of dichloromethane as a solvent, 0.5 mmol of the diimide coordination compound obtained in Application Example 7 and 0.5 mmol of $[\text{Ni}(\text{DME})\text{Br}_2]$ (where DME is dimethyl diethyl ether) were stirred at room temperature for 24 h, and the solvent was removed by vacuum concentration. The precipitate was washed with 50 mL of ethyl ether 3-5 times and dried under vacuum to obtain 0.3 g of an α -diimide nickel-based catalyst $\text{C}_{28}\text{H}_{34}\text{N}_2\text{NiBr}_2$ at a yield of 96%.

Application Example 12: Preparation of an α -diimide nickel-based catalyst containing two alkenyl groups

The preparation of the catalyst was conducted under oxygen-free, water-free conditions with protection of high-purity argon. With 40 mL of dichloromethane as a solvent, 1 mmol of the diimide coordination compound obtained in Application Example 8 and 1 mmol of $[\text{Ni}(\text{DME})\text{Cl}_2]$ (where DME is dimethyl diethyl ether) were stirred at room temperature for 72 h, and the solvent was removed by vacuum concentration. The precipitate was washed with 50 mL of ethyl ether 3-5 times and dried under vacuum to obtain 0.7 g of an α -diimide nickel-based catalyst $\text{C}_{42}\text{H}_{64}\text{N}_2\text{NiCl}_2$ at a yield of 92%.

Application Example 13: Preparation of alkenylcyclopentadiene

In a glass Schlenk flask, 100 mL of 33% NaOH, 0.5 mol of cyclopentadiene, and 0.5 mol of allyl chloride were added in sequence. In the presence of 2 g of tetrabutylammonium bromide as a phase transition agent, it was stirred in an ice water bath for 2 h. After stirring at room temperature for 6 h, the oil phase was washed to neutrality, dried over anhydrous potassium

carbonate, and distilled under reduced pressure to obtain 36.75 [g] of allyl cyclopentadiene at a yield of 70.0%.

Application Example 14: Preparation of alkenylcyclopentadiene

In a glass Schlenk flask, 120 mL of 33% NaOH, 0.6 mol of cyclopentadiene, and 0.5 mol of 3-bromo-1-butene were added in sequence. In the presence of 3 g of tetrabutylammonium bromide as a phase transition agent, it was stirred in an ice water bath for 2 h. After stirring at room temperature for 7 h, the oil phase was washed to neutrality, dried over anhydrous potassium carbonate, and distilled under reduced pressure to obtain 26.78 g of 3-cyclopentadiene-1-butene at a yield of 45.01%.

Application Example 15: Preparation of an alkenyl metallocene catalyst

Allylcyclopentadiene 4.14 mmol was added to a tetrahydrofuran solution. Equimolar n-BuLi was added dropwise while in an ice salt bath. It was stirred at room temperature for 2 h. A tetrahydrofuran solution containing equimolar ZrCl_4 was then added slowly. The solution exhibited a dark red color. The reaction was conducted by stirring at room temperature for 6 h. The solvent was distilled off. Toluene was added and the lithium salt was removed. The supernatant solution was drawn off to dryness. Washing was carried out with hexane several times to obtain 0.574 g of the product $\text{C}_{16}\text{H}_{16}\text{ZrCl}_2$ at a yield of 75%.

Application Example 16: Preparation of an alkenyl metallocene catalyst

3-Cyclopentadiene-1-butene 2.17 mmol and allylcyclopentadiene 2.17 mmol were added to a tetrahydrofuran solution. n-BuLi 4.34 mmol was added dropwise under conditions of an ice salt bath. It was stirred at room temperature for 3 h. A tetrahydrofuran solution containing equimolar TiCl_4 was then added slowly. The solution exhibited a dark red color. The reaction was conducted by stirring at room temperature for 8 h. The solvent was distilled off. Toluene was added and the lithium salt was removed. The supernatant solution was drawn off to dryness. Washing was carried out with hexane several times to obtain 0.444 g of the product $\text{C}_{17}\text{H}_{18}\text{TiCl}_2$ at a yield of 60%.

Application Example 17: Preparation of Component A of the polymerized double active site olefin polymerization catalyst

Under oxygen-free, water-free conditions, 2 mmol of the "post-metallocene" α -diimide nickel-based catalyst $\text{C}_{42}\text{H}_{48}\text{N}_2\text{NiBr}_2$ containing an alkenyl group obtained in Application Example 9, 2 mmol of the metallocene zirconium catalyst $\text{C}_{16}\text{H}_{16}\text{ZrCl}_2$ containing an alkenyl group obtained in Application Example 15, 5 mL of styrene, and 0.05 g of

2,2'-azobisisobutyronitrile were added in sequence to distilled toluene, thoroughly mixed, and then copolymerized in an oil bath at 80°C for 12 h. It was concentrated under heat. With normal hexane as a precipitating agent, a solid powder was obtained. It was washed with normal hexane 3-5 times and dried under vacuum to obtain the catalyst Component A, $P[(C_{42}H_{48}N_2NiBr_2)\text{-co-S-co-}(C_{16}H_{16}ZrCl_2)]$. The measured nickel content was 0.216 wt%, and the zirconium content was 0.444 wt%.

Application Example 18: Preparation of Component A of the polymerized double active site olefin polymerization catalyst

Under oxygen-free, water-free conditions, 10 mmol of the "post-metallocene" α -diimide nickel-based catalyst $C_{36}H_{52}N_2NiBr_2$ containing an alkenyl group obtained in Application Example 10, 10 mmol of the metallocene zirconium catalyst $C_{17}H_{18}ZrCl_2$ containing an alkenyl group obtained in Application Example 16, 10 mL of styrene, and 0.14 g of 2,2'-azobisisobutyronitrile were added in sequence to distilled toluene, thoroughly mixed, and then copolymerized in an oil bath at 80°C for 12 h. It was concentrated under heating. With normal hexane as a precipitating agent, a solid powder was obtained. It was washed with normal hexane 3-5 times and dried under vacuum to obtain the catalyst Component A, $P[(C_{36}H_{52}N_2NiBr_2)\text{-co-S-co-}(C_{17}H_{18}ZrCl_2)]$. The measured nickel content was 0.201 wt%, and the zirconium content was 0.532 wt%.

Application Example 19: Preparation of the polymerized double active site olefin polymerization catalyst supported on silicon dioxide

Under oxygen-free, water-free conditions, 5 g of silicon dioxide were weighed, dried under vacuum for 12 h, and then 5 mL of styrene and 0.5 mL of divinyl benzene were added to it. It was prepolymerized at 70[°C] for 20 min. Then, 2 mmol of the "post-metallocene" α -diimide nickel-based catalyst $C_{42}H_{48}N_2NiBr_2$ containing an alkenyl group obtained in Application Example 9, 2 mmol of the metallocene zirconium catalyst $C_{16}H_{16}ZrCl_2$ containing an alkenyl group obtained in Application Example 15, and 0.05 g of 2,2'-azobisisobutyronitrile were added in sequence to distilled toluene, thoroughly mixed, and then copolymerized in an oil bath at 80°C for 12 h. It was concentrated under heat to remove the solvent. The precipitate was washed with normal hexane 3-5 times and dried under vacuum to obtain the catalyst Component A, $SiO_2\text{-}P[(C_{42}H_{48}N_2NiBr_2)\text{-co-S-co-}(C_{16}H_{16}ZrCl_2)]$. The measured nickel content was 0.153 wt%, and the zirconium content was 0.387 wt%.

Application Example 20: Preparation of the polymerized double active site olefin polymerization catalyst supported on silicon dioxide

Under oxygen-free, water-free conditions, 10 g of silicon dioxide were weighed, dried under vacuum for 12 h, and then 10 mL of styrene and 1 mL of divinyl benzene were added to it. It was prepolymerized at 70[°C] for 20 min. Then, 10 mmol of the “post-metallocene” α -diimide nickel-based catalyst $C_{36}H_{52}N_2NiBr_2$ containing an alkenyl group obtained in Application Example 10, 10 mmol of the metallocene zirconium catalyst $C_{17}H_{18}ZrCl_2$ containing an alkenyl group obtained in Application Example 16, and 0.14 g of 2,2'-azobisisobutyronitrile were added in sequence to distilled toluene, thoroughly mixed, and then copolymerized in an oil bath at 80°C for 12 h. It was concentrated under heat to remove the solvent. The precipitate was washed with normal hexane 3-5 times and dried under vacuum to obtain the catalyst Component A, $SiO_2-P[(C_{36}H_{52}N_2NiBr_2)-co-S-co-(C_{17}H_{18}ZrCl_2)]$. The measured nickel content was 0.198 wt%, and the zirconium content was 0.479 wt%.

Application Example 21: Homogeneous and heterogeneous polymerization of ethylene

Ethylene polymerization was conducted under water-free and oxygen-free conditions. 50 mL of toluene, 0.45 mL of methylaluminoxane, and 1.136 μ mol (according to $Al/M = 500$) of the polymerized catalyst obtained in Application Example 17 were added to the reactor in sequence. Ethylene was reacted at 20°C for 0.5 h. The reaction was terminated with an ethanol solution containing 1 wt% hydrochloric acid. The obtained product was filtered, washed with ethanol 3 times, and dried under vacuum at 40°C for 24 h to obtain 0.137 g of polyethylene. The activity was 2.41×10^5 g PE/(mol Ni·h).

Application Example 22: Homogeneous and heterogeneous polymerization of ethylene

By the same operation as in Application Example 19 and with 2.0 mL of methylaluminoxane (according to $Al/Ni = 4000$), 0.14 g of polyethylene was obtained. The activity was 2.54×10^5 g PE/(mol Ni·h).

Application Example 23: Homogeneous and heterogeneous polymerization of ethylene

By the same operation as in Application Example 19 and with 0.9 mL of methylaluminoxane (according to $Al/Ni = 1743$), 0.42 g of polyethylene was obtained by polymerization at 70°C. The activity was 3.47×10^6 g PE/(mol Ni·h).

Application Example 24: Homogeneous and heterogeneous polymerization of ethylene

Ethylene polymerization was conducted under water-free and oxygen-free conditions. 50 mL of toluene, 0.45 mL of methylaluminoxane, and 1.136 μ mol (according to $Al/M = 500$) of

the polymerized catalyst obtained in Application Example 19 were added to the reactor in sequence. Ethylene was reacted at 20°C for 0.5 h. The reaction was terminated with an ethanol solution containing 1 wt% hydrochloric acid. The obtained product was filtered, washed with ethanol 3 times, and dried under vacuum at 40°C for 24 h to obtain 0.10 g of polyethylene. The activity was 1.72×10^5 g PE/(mol Ni·h).

Application Example 25: Homogeneous and heterogeneous polymerization of ethylene

By the same operation as in Application Example 22 and with 2.0 mL of methylaluminoxane (according to Al/Ni = 4000), 0.183 g of polyethylene was obtained. The activity was 3.22×10^5 g PE/(mol Ni·h).

Application Example 26: Homogeneous and heterogeneous polymerization of ethylene

By the same operation as in Application Example 22 and polymerization at 50°C, 0.255 g of polyethylene was obtained. The activity was 2.24×10^5 g PE/(mol Ni·h).

Application Example 27: Homogeneous and heterogeneous polymerization of ethylene

By the same operation as in Application Example 22 and polymerization at 50°C under 7 atm, 1.7 g of polyethylene were obtained. The activity was 3.0×10^6 g PE/(mol Ni·h).

Application Example 28: Homogeneous and heterogeneous polymerization of ethylene

By the same operation as in Application Example 25 and polymerization at 12°C under an ethylene pressure of 20 atm, 7.31 g of polyethylene were obtained. The activity was 1.11×10^7 g PE/(mol Ni·h).

[19] 中华人民共和国国家知识产权局

[51] Int. Cl⁷

C08F 10/02

C08F 4/70

[12] 发明专利申请公开说明书

[21] 申请号 02104276.4

[43] 公开日 2002 年 10 月 2 日

[11] 公开号 CN 1371924A

[22] 申请日 2002.3.4 [21] 申请号 02104276.4

[71] 申请人 中国科学院长春应用化学研究所

地址 130022 吉林省长春市人民大街 159 号

[72] 发明人 金国新 张 道 车晓明

权利要求书 4 页 说明书 13 页 附图页数 0 页

[54] 发明名称 高分子化镍钴双活性中心烯烃聚合催化剂

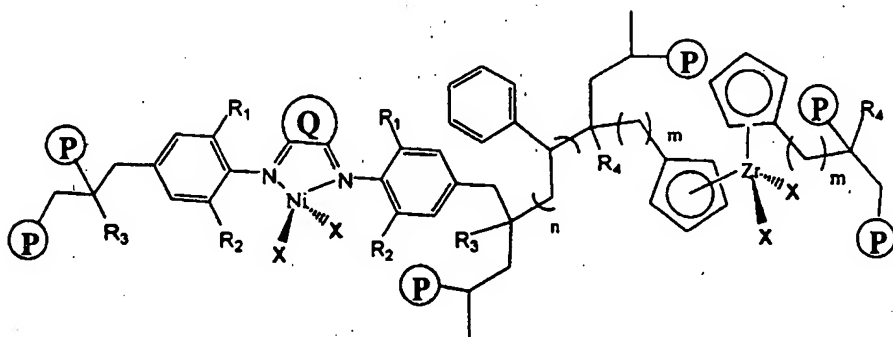
[57] 摘要

本发明属于高分子化双活性中心烯烃聚合催化剂的制备和催化烯烃聚合。催化剂由 A 和 B 两组分组成, A 组分表达式为 $[P(\text{ComNi} - \text{co} - \text{S} - \text{co} - \text{ComZr})]$ 或 $[\text{SiO}_2 - P(\text{ComNi} - \text{co} - \text{S} - \text{co} - \text{ComZr})]$, P 表示共聚物, S 为苯乙烯, co 表示共聚, ComNi 表示含有烯烃基团的“茂后” α -双亚胺镍基催化剂, ComZr 表示含有烯烃基团的茂钴催化剂。 $[P(\text{ComNi} - \text{co} - \text{S} - \text{co} - \text{ComZr})]$ 是由 α -双亚胺镍催化剂和茂金属催化剂与苯乙烯的共聚物, SiO_2 表示二氧化硅载体化。 B 组份为甲基铝氧烷(MAO), 改进的甲基铝氧烷(MMAO)或五氟苯硼 $[\text{B}(\text{C}_6\text{F}_5)_3]$ 其中任意一种。这类催化剂催化乙烯聚合具有较高的活性, 适合气相和淤浆聚合工艺, 聚合物不含无机灰分。

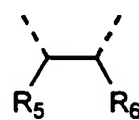
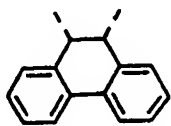
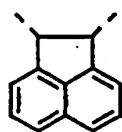
ISSN 1008-4274

权 利 要 求 书

1. 一种高分子化的镍锆双活性中心烯烃聚合催化剂由 A 和 B 两组分组成, 其特征在于 A 组分表达式为 $[P(Com Ni - co - S - co - Com Zr)]$ 或 $[SiO_2 - P(Com Ni - co - S - co - Com Zr)]$, P 表示共聚物, S 为聚苯乙烯, co 表示共聚, ComNi 表示含有烯烃基团的“茂后” α -双亚胺镍基催化剂, ComZr 表示含有烯烃基团的茂锆金属类催化剂, $[P(Com Ni - co - S - co - Com Zr)]$ 是由 α -双亚胺镍催化剂和茂金属催化剂与苯乙烯的共聚物, 它具有如下结构:



其中 m 是 0-4 的整数; n 是 0-100 之间的整数; X 为 Cl 或 Br; R_1 与 R_2 可以相同或不同, 分别为氢、甲基、异丙基或叔丁基; R_3 为氢、甲基、丙基或丁基的任意一种; R_4 为氢或甲基; Q 是选自下述环状化合物的二价残基或其混合物:

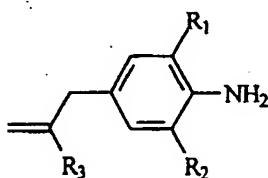


其中, R_5 与 R_6 可以相同或不同, 分别为甲基、乙基、丙基或杂环: SiO_2

表示二氧化硅载体化。B 组份为甲基铝氧烷(MAO)、改进甲基铝氧烷(MMAO)或五氟苯硼[$B(C_6F_5)_3$]其中任意一种。

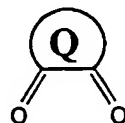
2. 一种制备权利要求 1 所述的高分子化的镍钴双活性中心烯烃聚合催化剂 A 组分的方法, 包括:

取代芳胺和烯烷基氯基或烯烷基溴生成的 N-烯烷基苯胺在无水氯化锌存在下重排, 得到 4-烯烷基芳胺, 产率 25-71%:

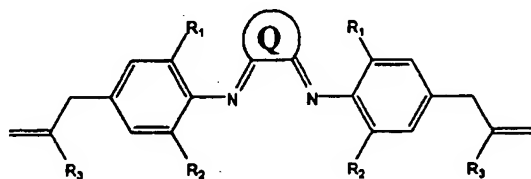


其中 R_1 与 R_2 可以相同或不同, 分别为 H、甲基、异丙基或叔丁基, R_3 为 H, 甲基, 乙基, 丙基或丁基;

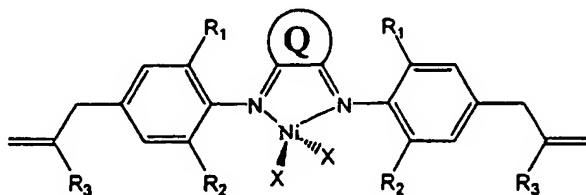
在甲酸、乙酸、三氟乙酸和盐酸的催化下, 在酸和醇溶剂体系中与下式所示的 α -二酮进行缩合反应



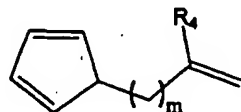
得到下式所示的含有烯烷基团的 α -双亚胺配体, 产率 72-84%;



在无水无氧条件下, 将上述配体与 NiX_2 , 其中 X 为 Cl 或 Br, 配位反应, 得到下式含有烯烷基团的 α -双亚胺 Ni(II) 配合物, 产率 92-98%;

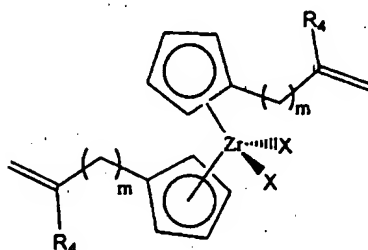


以四丁基溴化铵为相转移剂，环戊二烯与卤代烯烃作用得到以下烯烷基环戊二烯，产率 40-70%：



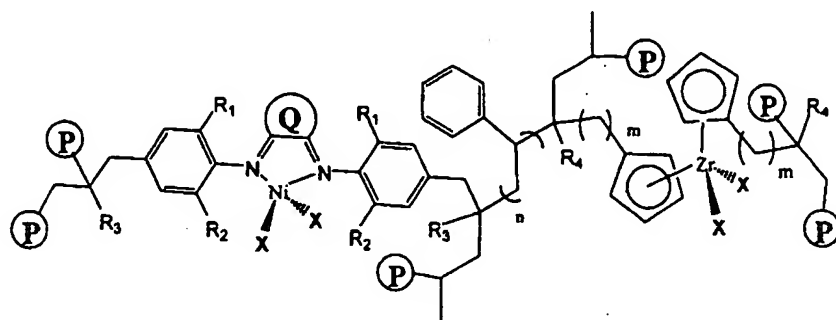
其中 m 为 0-4 的整数， R_4 为氢或甲基；

在四氢呋喃体系中，用等摩尔数的 $n\text{-BuLi}$ 处理上述烯烷基环戊二烯，与等当量的 ZrCl_4 反应，得到如下烯烷基茂金属催化剂，产率 60-75%；

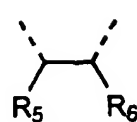
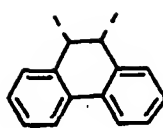
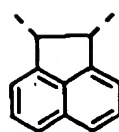


其中 X 为 Cl 或 Br ； m 为 0-4 的整数； R_4 为氢或甲基；

在无水无氧条件下，将含有烯烷基团的 α -双亚胺 $\text{Ni}(\text{II})$ 配合物和含有烯烷基的茂金属催化剂在 AIBN，AIBN 为偶氮异丁乙晴，引发下与苯乙烯共聚，使得催化剂通过 σ 键与聚乙烯链连结，得到如下式的高分子化双活性烯烷基聚合催化剂：



其中 m 是 0-4 的整数； n 是 0-100 之间的整数； X 为 Cl 或 Br ； R_1 与 R_2 可以相同或不同，分别为氢、甲基、异丙基或叔丁基； R_3 为氢、甲基、丙基或丁基的任意一种； R_4 为氢或甲基； Q 是选自下述环状化合物的二价残基或其混合物：



其中, R_5 与 R_6 可以相同或不同, 分别为甲基、乙基、丙基或杂环; SiO_2 表示二氧化硅载体将高分子化催化剂 $[P(Com-Ni-co-S-co-Com-Zr)]$ 固载化;

A 组分在助催化剂 B 组份, B 组份为甲基铝氧烷(MAO)、改进甲基铝氧烷(MMAO)或五氟苯硼 $[B(C_6F_5)_3]$ 的作用下, 在 1-20 个大气压下催化烯烃聚合, 活性数量级为 $10^5-10^7 gPE(molNi \cdot h)^{-1}$ 。

3. 如权利要求 1、2 所述的高分子化的镍钴双活性中心烯烃聚合催化剂制备方法, 其特征在于二氧化硅负载的高分子化 α -双亚胺镍基催化剂 A 组分的制备过程中, 先加入二氧化硅载体、溶剂和催化剂, 待温度升至 $70 \pm 0.5^\circ C$ 后加入引发剂, 于 $80 \pm 0.5^\circ C$ 保温聚合 8 小时。

4. 如权利要求 1 所述的高分子化的“茂后” α -双亚胺镍基烯烃聚合催化剂的制备方法, 其特征在于生产聚乙烯过程中, 包括使用权利要求 1 所示的高分子化的镍钴双活性中心烯烃聚合催化剂 A 组分的步骤。

5. 如权利要求 1 所述的高分子化的镍钴双活性中心烯烃聚合催化剂的制备方法, 其特征在于生产聚乙烯的聚合压力为 1-20 atm。

6. 如权利要求 1 所述的高分子化的镍钴双活性中心烯烃聚合催化剂的制备方法, 其特征在于生产聚乙烯采用均相聚合和非均相聚合。

说明书

高分子化镍钴双活性中心烯烃聚合催化剂

技术领域：本发明涉及一种烯烃聚合催化剂，具体的涉及一种含有镍钴双活性中心的高分子化烯烃聚合催化剂；

本发明还涉及一种上述催化剂的制备方法；

本发明还涉及上述催化剂在烯烃聚合中，尤其是在乙烯聚合中的应用。

背景技术：起始于上个世纪末的“茂后”后过渡金属催化剂被誉为继 Ziegler-Natta 催化剂和茂金属催化剂之后的第三代高活性烯烃聚合催化剂，现已成为世界范围内新型烯烃聚合催化剂的研究热点。但是传统前过渡金属催化剂在现代工业生产中正发挥着巨大的作用，如何结合前过渡金属催化剂和后过渡金属催化剂的优点以制备结构和性能新颖的聚烯烃材料成为目前烯烃聚合重要的研究方向。中国专利(98125651.1, 1998; 01140470.1, 2001)分别公开了高分子化茂金属烯烃聚合催化剂的制备方法和高分子化后过渡金属“茂后”镍基烯烃聚合催化剂的制备方法。有关高分子化的镍钴双活性中心催化剂尚未见报道，这一工作对获取理想分子量和支化度的聚合物，适应工业化生产装置，提高聚合物的物理加工性能等方面有一定的意义。

发明内容：本发明的目的是提供一种高分子化的镍钴双活性中心烯烃聚合催化剂；

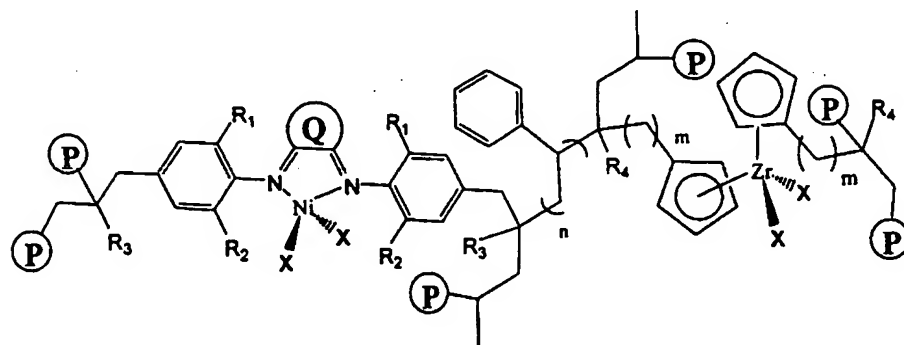
本发明的另一目的是提供一种高分子化的镍钴双活性中心烯烃聚合催化剂的制备方法，该方法采用含烯烃取代基团的 IVB 族茂

金属化合物和 α -双亚胺镍基化合物在引发剂作用下与苯乙烯共聚，将前后过渡金属催化剂通过 σ 键连接到高分子链上形成高分子化的镍钴双活性中心烯烃聚合催化剂；

本发明的第三个目的是提供一种高分子化的镍钴双活性中心催化剂在烯烃聚合，尤其在乙烯聚合中的应用。

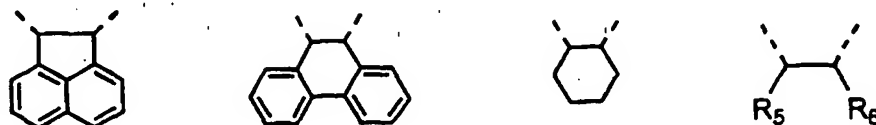
高分子化的镍钴双活性中心催化剂对烯烃聚合同样具有很高的催化活性，而且将前后过渡金属催化剂高分子化可以很容易地控制催化剂在分子链上的组成、分布，通过调节催化剂在分子链上的分布可以最大限度地发挥活性中心的催化作用，达到改进聚合物的物理机械和加工性能。另外，高分子化镍钴双活性中心催化剂催化烯烃聚合所得到的聚合物不含无机灰分。

本发明制备的催化剂由 A 和 B 两组分组成，A 组分表达式为 $[P(ComNi-co-S-co-ComZr)]$ 或 $[SiO_2-P(ComNi-co-S-co-ComZr)]$ ，P 表示共聚物，S 为聚苯乙烯，co 表示共聚，ComNi 表示含有烯烃基团的“茂后” α -双亚胺镍基催化剂，ComZr 表示含有烯烃基团的茂钴金属类催化剂。 $[P(ComNi-co-S-co-ComZr)]$ 是由 α -双亚胺镍催化剂和茂金属催化剂与苯乙烯的共聚物，它具有如下结构：



其中 m 是 0-4 的整数； n 是 0-100 之间的整数； X 为 Cl 或 Br； R_1 与 R_2 可以相同或不同，分别为氢、甲基、异丙基或叔丁基； R_3 为氢、甲基、

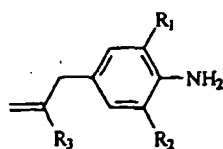
丙基或丁基的任意一种； R_3 为氢或甲基；Q是选自下述环状化合物的二价残基或其混合物：



其中， R_5 与 R_6 可以相同或不同，分别为甲基、乙基、丙基或杂环； SiO_2 表示二氧化硅载体将高分子化催化剂 $[P(Com\ Ni-co-S-co-Com\ Zr)]$ 固载化。B组份为甲基铝氧烷(MAO)、改进甲基铝氧烷(MMAO)或五氟苯硼 $[B(C_6F_5)_3]$ 其中任意一种。

催化剂的制备过程如下：

取代芳胺和烯烷基氯基或烯烷基溴生成的N-烯烷基苯胺在无水氯化锌存在下重排，得到4-烯烷基芳胺，产率25-71%。

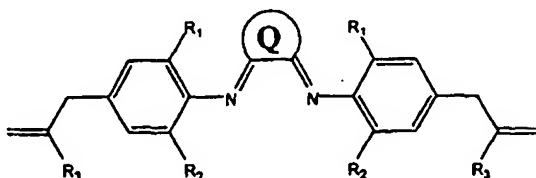


其中 R_1 与 R_2 可以相同或不同，分别为H、甲基、异丙基或叔丁基， R_3 为H，甲基，乙基，丙基或丁基。

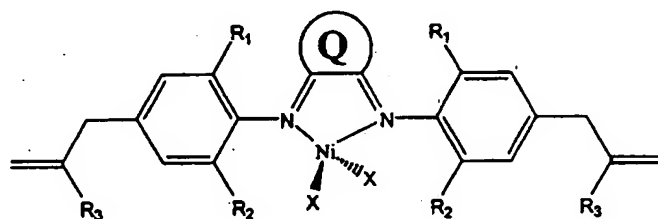
在甲酸、乙酸、三氟乙酸和盐酸的催化下，在酸和醇溶剂体系中与下式所示的 α -二酮进行缩合反应



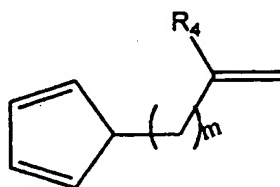
得到下式所示的含有烯烷基团的 α -双亚胺配体，产率72-84%；



在无水无氧条件下, 进行上述配体与 NiX_2 , 其中 X 为 Cl 或 Br, 的配位反应, 得到下式含有烯烃基团的 α -双亚胺 Ni(II) 配合物, 产率 92—98%;

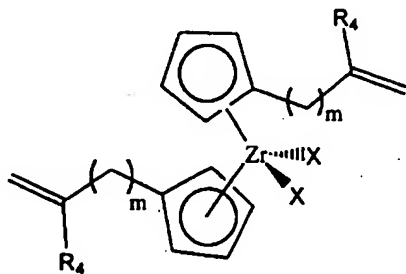


以四丁基溴化铵为相转移剂, 环戊二烯与卤代烯烃作用得到以下烯烃基环戊二烯, 产率 40-70%:



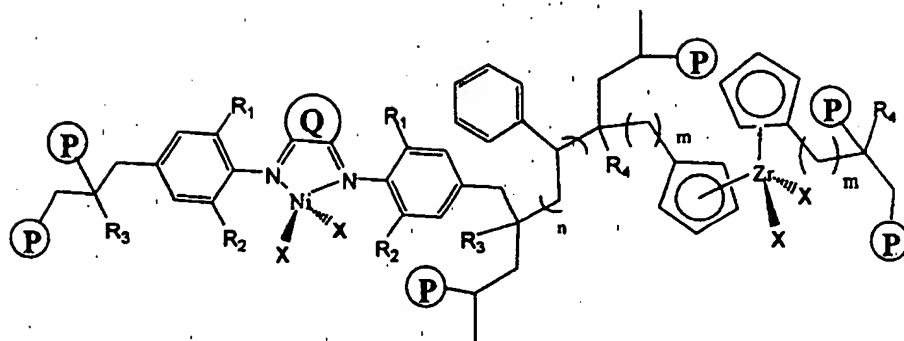
其中 m 为 0-4 的整数, R_4 为氢或甲基。

在四氢呋喃体系中, 用等摩尔数的 $n\text{-BuLi}$ 处理上述烯烃基环戊二烯, 与等当量的 ZrCl_4 反应, 得到如下烯烃基茂金属催化剂, 产率 60-75%。

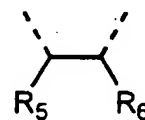
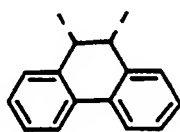
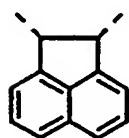


其中 X 为 Cl 或 Br; m 为 0-4 的整数; R_4 为氢或甲基。

在无水无氧条件下, 将含有烯烃基团的 α -双亚胺 Ni(II) 配合物和含有烯烃的茂金属催化剂在 AIBN, AIBN 为偶氮异丁乙晴, 引发下与苯乙烯共聚, 使得催化剂通过 σ 键与聚乙烯链连结, 得到如下式的高分子化双活性烯烃聚合催化剂:



其中 m 是 0-4 的整数； n 是 0-100 之间的整数； X 为 Cl 或 Br； R_1 与 R_2 可以相同或不同，分别为氢、甲基、异丙基或叔丁基； R_3 为氢、甲基、丙基或丁基的任意一种； R_4 为氢或甲基； Q 是选自下述环状化合物的二价残基或其混合物：



其中， R_5 与 R_6 可以相同或不同，分别为甲基、乙基、丙基或杂环； SiO_2 表示二氧化硅载体将高分子化催化剂 $[P(Com\ Ni-co-S-co-Com\ Zr)]$ 固载化。

A 组分在助催化剂 B 组份，B 组份为甲基铝氧烷(MAO)、改进甲基铝氧烷(MMAO)或五氟苯硼 $[B(C_6F_5)_3]$ 的作用下，在 1-20 个大气压下催化烯烃聚合，活性数量级为 $10^5-10^7 gPE(molNi \cdot h)^{-1}$ 。

具体实施方式如下：

实施例 1：烯丙基类芳胺的制备

将 2,6-二异丙基苯胺 0.2 摩尔和烯丙基氯 0.1 摩尔加热回流 8 小时，冷却放置过夜，倾入 400 毫升水中，用氢氧化钠溶液碱化，乙醚萃

取, 真空减压蒸馏得 N-烯丙炔基-2, 6-二异丙基苯胺 18.33 克, 产率为 84%。以 100 毫升甲苯为溶剂加入 N-烯丙炔基-2, 6-二异丙基苯胺 0.084 摩尔和无水氯化锌 0.1 摩尔, 氩气气氛下回流 5 小时, 冷却后倾入氢氧化钠水溶液中碱化, 分离出有机层, 下层不溶物溶于热的浓盐酸中, 再倾入上述乙醚萃取液中, 无水硫酸镁干燥, 真空浓缩后减压蒸馏得 4-烯丙炔基-2, 6-二异丙基苯胺 12.92 克, 产率为 71%。

实施例 2: 烯丙基类芳胺的制备

将 2-特丁基苯胺 0.1 摩尔和 1-溴-2-丁烯炔基 0.05 摩尔加热回流 10 小时, 冷却放置过夜, 倾入 200 毫升水中, 用氢氧化钠溶液碱化, 乙醚萃取, 真空减压蒸馏得 N-(2-甲基丙烯基)-2-特丁基苯胺 5.35 克, 产率 53%。以 200 毫升甲苯为溶剂加入 N-(2-甲基丙烯基)-2-特丁基苯胺 0.2 摩尔和无水氯化锌 0.2 摩尔, 氩气气氛下回流 8 小时, 冷却后倾入氢氧化钠水溶液中碱化, 分离出有机层, 下层不溶物溶于热的浓盐酸中, 再倾入上述乙醚萃取液中, 无水硫酸镁干燥, 真空浓缩后减压蒸馏得 4-(2-甲基丙烯基)-2-特丁基苯胺 24.89 克, 产率 61%。

实施例 3: 烯丙基类芳胺的制备

将 2, 6-二甲基苯胺 0.12 摩尔和 1-溴-2-戊烯 0.06 摩尔加热回流 9 小时, 冷却放置过夜, 倾入 300 毫升水中, 用氢氧化钠溶液碱化, 乙醚萃取, 真空减压蒸馏得 N-(2-乙基丙烯基)-2, 6-二甲基苯胺 3.72 克, 产率为 33%。以 80 毫升甲苯为溶剂加入 N-(2-乙基丙烯基)-2, 6-二甲基苯胺 0.05 摩尔和无水氯化锌 0.05 摩尔, 氩气气氛下回流 7 小时, 冷却后倾入氢氧化钠水溶液中碱化, 分离出有机层, 下层不溶物溶于热的浓盐酸中, 再倾入上述乙醚萃取液中, 无水硫酸镁干燥, 真空浓缩后减压得 4-烯丙炔基-2, 6-二甲基苯胺 2.77 克, 产率为 29%。

实施例 4: 烯丙基类芳胺的制备

将 2,6-二异丙基苯胺 0.1 摩尔和 1-溴-2-庚烯 0.05 摩尔加热回流 10 小时, 冷却放置过夜, 倾入 300 毫升水中, 用氢氧化钠溶液碱化, 乙醚萃取, 真空减压蒸馏得 N-(2-丁基丙烯基)-2,6-二异丙基苯胺 4.09 克. 产率为 30%。以 50 毫升甲苯为溶剂加入 N-(2-丁基丙烯基)-2,6-二异丙基苯胺 0.05 摩尔和无水氯化锌 0.05 摩尔, 氩气气氛下回流 8 小时, 冷却后倾入氢氧化钠水溶液中碱化, 分离出有机层, 下层不溶物溶于热的浓盐酸中, 再倾入上述乙醚萃取液中, 无水硫酸镁干燥, 真空浓缩后减压蒸馏得 4-(2-丁基烯丙基)-2,6-二异丙基苯胺 3.44 克, 产率为 25%。

实施例 5: 含有两个烯烃基团的双亚胺双齿配体的制备

2 毫摩尔 α -萘酮与 4 毫摩尔 4-烯丙基-2,6-二异丙基苯胺溶于 20 毫升乙酸中, 加热回流 1 小时后, 冷却到室温, 得到固体沉淀, 过滤, 依此用乙酸洗涤 (3×20 毫升)、正己烷洗涤 (3×20 毫升), 真空干燥, 即得 α -双亚胺配体化合物 $C_{42}H_{48}N_2$ 1.0 g, 产率 84%。

实施例 6: 含有两个烯烃基团的双亚胺双齿配体的制备

3 毫摩尔 α -丁二酮与 6 毫摩尔 4-(2-甲基烯丙基)-2-特丁基苯胺溶于 30 毫升甲醇中, 加 3-5 滴甲酸作催化剂, 加热回流 1 小时后, 冷却到室温, 得到固体沉淀, 过滤, 依此用甲醇洗涤 (3×20 毫升)、正己烷洗涤 (3×20 毫升), 真空干燥, 即得 α -双亚胺配体化合物 $C_{36}H_{52}N_2$ 1.2 g, 产率 80%。

实施例 7: 含有两个烯烃基团的双亚胺双齿配体的制备

2.5 毫摩尔 α -环己二酮与 5 毫摩尔 4-烯丙基-2,6-二甲基苯胺溶于 25 毫升乙醇中, 加 3-5 滴盐酸作催化剂, 加热回流 1 小时

后，冷却到室温，得到固体沉淀，过滤，依此用乙醇洗涤（3×20 毫升）、正己烷洗涤（3×20 毫升），真空干燥，即得 α -双亚胺配体化合物 $C_{28}H_{34}N_2$ 1.0 g，产率 72%。

实施例 8：含有两个烯烃基团的双亚胺双齿配体的制备

2.5 毫摩尔 α -菲二酮与 5 毫摩尔 4-(2-丁基烯丙基)-2,6-二异丙基苯胺溶于 30 毫升甲醇中，加热回流 1 小时后，冷却到室温，得到固体沉淀，过滤，依此用甲醇洗涤（3×20 毫升）、正己烷洗涤（3×20 毫升），真空干燥，即得 α -双亚胺配体化合物 $C_{52}H_{66}N_2$ 1.5 g，产率 82%。

实施例 9：含有两个烯烃基团的 α -双亚胺镍基催化剂的制备

催化剂的制备在无氧无水及高纯氩气保护条件下进行。以 30ml 二氯甲烷为溶剂，将实施例 5 中得到的二亚胺配体 1mmol 与 1mmol $[Ni(DME)Br_2]$ (DME:二甲基乙二醚)在室温下搅拌 12 小时，真空浓缩除去溶剂，用 50ml 乙醚洗涤沉淀 3-5 次，真空干燥，得 α -双亚胺镍基催化剂 $C_{42}H_{48}N_2NiBr_2$ 0.8g，产率 98%。

实施例 10：含有两个烯烃基团的 α -双亚胺镍基催化剂的制备

催化剂的制备在无氧无水及高纯氩气保护条件下进行。以 40ml 二氯甲烷为溶剂，将实施例 6 中得到的二亚胺配体 1mmol 与 1mmol $[Ni(DME)Cl_2]$ (DME:二甲基乙二醚)在室温下搅拌 48 小时，真空浓缩除去溶剂，用 50ml 乙醚洗涤沉淀 3-5 次，真空干燥，得 α -双亚胺镍基催化剂 $C_{36}H_{52}N_2NiCl_2$ 0.6g，产率 98%。

实施例 11：含有两个烯烃基团的 α -双亚胺镍基催化剂的制备

催化剂的制备在无氧无水及高纯氩气保护条件下进行。以 30ml 二氯甲烷为溶剂，将实施例 7 中得到的二亚胺配体 0.5mmol 与

0.5mmol $[\text{Ni}(\text{DME})\text{Br}_2]$ (DME:二甲基乙二醚)在室温下搅拌 24 小时,真空浓缩除去溶剂,用 50ml 乙醚洗涤沉淀 3-5 次,真空干燥,得 α -双亚胺镍基催化剂 $\text{C}_{28}\text{H}_{34}\text{N}_2\text{NiBr}_2$ 0.3g, 产率 96%。

实施例 12: 含有两个烯烃基团的 α -双亚胺镍基催化剂的制备

催化剂的制备在无氧无水及高纯氩气保护条件下进行。以 40ml 二氯甲烷为溶剂,将实施例 8 中得到的二亚胺配体 1mmol 与 1mmol $[\text{Ni}(\text{DME})\text{Cl}_2]$ (DME:二甲基乙二醚)在室温下搅拌 72 小时,真空浓缩除去溶剂,用 50ml 乙醚洗涤沉淀 3-5 次,真空干燥,得 α -双亚胺镍基催化剂 $\text{C}_{42}\text{H}_{64}\text{N}_2\text{NiCl}_2$ 0.7g, 产率 92%。

实施例 13 烯烃基环戊二烯的制备

在玻璃 Schlenk 瓶中依次加入 100mL 的 33%的 NaOH, 0.5mol 环戊二烯, 0.5mol 烯丙基氯, 在 2g 四丁基溴化铵为相转移剂下, 冰水浴中搅拌 2 小时, 室温下搅拌 6 小时之后, 油相洗至中性, 采用无水碳酸钾干燥后, 减压蒸馏下得到烯丙基环戊二烯 36.75。产率 70.0%。

实施例 14 烯烃基环戊二烯的制备

在玻璃 Schlenk 瓶中依次加入 120mL 的 33%的 NaOH, 0.6mol 环戊二烯, 0.5mol 3-溴 1-丁烯, 在 3g 四丁基溴化铵为相转移剂下, 冰水浴中搅拌 2 小时, 室温下搅拌 7 小时之后, 油相洗至中性, 采用无水碳酸钾干燥后, 减压蒸馏下得到 3-环戊二烯基-1-丁烯 26.78g。产率 45.01%。

实施例 15 烯烃基茂金属催化剂的制备

将烯丙基环戊二烯 4.14mmol 加入到四氢呋喃溶液中, 在冰盐浴的条件下, 滴加等摩尔数的 $n\text{-BuLi}$, 在室温下搅拌 2 小时, 然后缓慢地加入含等当量的 ZrCl_4 的四氢呋喃溶液, 溶液呈深红

色，室温下搅拌反应 6 小时，蒸去溶剂，加入甲苯离心除去锂盐，将清液抽干，再用己烷洗涤数次即得产物 $C_{16}H_{16}ZrCl_2$ 0.574g，产率 75%。

实施例 16 烯烷基茂金属催化剂的制备

将 3-环戊二烯基-1-丁烯 2.17mmol，烯丙基环戊二烯 2.17mmol 加入到四氢呋喃溶液中，在冰盐浴的条件下，滴加 4.34mmol 的 $n-BuLi$ ，在室温下搅拌 3 小时，然后缓慢地加入含等当量的 $TiCl_4$ 的四氢呋喃溶液，溶液呈深红色，室温下搅拌反应 8 小时，蒸去溶剂，加入甲苯离心除去锂盐，将清液抽干，再用己烷洗涤数次即得产物 $C_{17}H_{18}TiCl_2$ 0.444g，产率 60%。

实施例 17: 高分子化双活性中心烯烃聚合催化剂 A 组分的制备

在无氧无水条件下，将实施例 9 中得到的含有烯烷基团的“茂后” α -双亚胺镍基催化剂 $C_{42}H_{48}N_2NiBr_2$ 2mmol，实施例 15 中得到的含有烯烷基团的茂锆催化剂 $C_{16}H_{16}ZrCl_2$ 2mmol，苯乙烯 5ml，偶氮二异丁腈 0.05g，依次加入到蒸过的甲苯中混合均匀，然后在 80℃ 的油浴中共聚 12 小时。在加热条件下浓缩，用正己烷作沉淀剂，得固体粉末，再用正己烷洗涤 3 - 5 次，真空干燥，得催化剂 A 组分 $P[(C_{42}H_{48}N_2NiBr_2)-co-S-co-(C_{16}H_{16}ZrCl_2)]$ ，测定镍含量为 0.216wt%，锆的含量为 0.444wt %。

实施例 18: 高分子化双活性中心烯烃聚合催化剂 A 组分的制备

在无氧无水条件下，将实施例 10 中得到的含有烯烷基团的“茂后” α -双亚胺镍基催化剂 $C_{36}H_{52}N_2NiBr_2$ 10mmol，实施例 16 中得到的含有烯烷基团的茂锆催化剂 $C_{17}H_{18}ZrCl_2$ 10mmol，苯乙烯 10ml，偶氮二异丁腈 0.14g，依次加入到蒸过的甲苯中混合均匀，然后在 80℃ 的油浴中共聚 12 小时。在加热条件下浓缩，用正己烷作沉淀剂，

得固体粉末，再用正己烷洗涤 3 - 5 次，真空干燥，得催化剂 A 组分 $P[(C_{36}H_{52}N_2NiBr_2) - co - S - co - (C_{17}H_{18}ZrCl_2)]$ ，测定镍含量为 0.201wt %，锆的含量为 0.532wt %。

实施例 19: 二氧化硅负载的高分子化双活性烯烃聚合催化剂的制备

在无氧无水条件下，称取二氧化硅载体 5 克，真空干燥 12 小时后，加入苯乙烯 5ml 和二乙烯基苯 0.5ml，在 70 预聚 20 分钟，再将实施例 9 中得到的含有烯烃基团的“茂后” α -双亚胺镍基催化剂 $C_{42}H_{48}N_2NiBr_2$ 2mmol，实施例 15 中得到的含有烯烃基团的茂锆催化剂 $C_{16}H_{16}ZrCl_2$ 2mmol，偶氮二异丁腈 0.05g，依次加入到蒸过的甲苯中混合均匀，然后在 80℃ 的油浴中共聚 12 小时。在加热条件下浓缩抽去溶剂，沉淀用正己烷洗涤 3-5 次，真空干燥，得催化剂 A 组分 $SiO_2 - P[(C_{42}H_{48}N_2NiBr_2) - co - S - co - (C_{16}H_{16}ZrCl_2)]$ ，测定镍含量为 0.153wt %，锆的含量为 0.387wt %。

实施例 20: 二氧化硅负载的高分子化双活性烯烃聚合催化剂的制备

在无氧无水条件下，称取二氧化硅载体 10 克，真空干燥 12 小时后，加入苯乙烯 10ml 和二乙烯基苯 1ml，在 70 预聚 20 分钟，再将实施例 10 中得到的含有烯烃基团的“茂后” α -双亚胺镍基催化剂 $C_{36}H_{52}N_2NiBr_2$ 10mmol，实施例 16 中得到的含有烯烃基团的茂锆催化剂 $C_{17}H_{18}ZrCl_2$ 10mmol，偶氮二异丁腈 0.14g，依次加入到蒸过的甲苯中混合均匀，然后在 80℃ 的油浴中共聚 12 小时。在加热条件下浓缩抽去溶剂，沉淀用正己烷洗涤 3-5 次，真空干燥，得催化剂 A 组分 $SiO_2 - P[(C_{36}H_{52}N_2NiBr_2) - co - S - co - (C_{17}H_{18}ZrCl_2)]$ ，测定镍含量为 0.198wt %，锆的含量为 0.479wt %。

实施例 21: 乙烯均相和非均相聚合

乙烯聚合在无水无氧条件下进行，在反应体系中依此加入甲苯 50ml、甲基铝氧烷 0.45ml、由实施例 17 得到的高分子化催化剂 $1.136\mu\text{mol}$ （按 $\text{Al}/\text{M}=500$ ）、乙烯于 20°C 反应 0.5 小时，用含 1% 盐酸的乙醇溶液终止反应，将所得产物过滤，用乙醇洗涤 3 次，并于 40°C 真空干燥 24 小时，得聚乙烯 0.137 g，活性为 2.41×10^5 g PE/(mol Ni h)。

实施例 22：乙烯均相和非均相聚合

操作同实施例 19，甲基铝氧烷 2.0ml（按 $\text{Al}/\text{Ni}=4000$ ），得聚乙烯 0.14 g，活性为 2.54×10^5 g PE/(mol Ni h)。

实施例 23：乙烯均相和非均相聚合

操作同实施例 19，甲基铝氧烷 0.9ml（按 $\text{Al}/\text{Ni}=1743$ ）， 70°C 下聚合得聚乙烯 0.42 g，活性为 3.47×10^6 g PE/(mol Ni h)。

实施例 24：乙烯均相和非均相聚合

乙烯聚合在无水无氧条件下进行，在反应体系中依此加入甲苯 50ml、甲基铝氧烷 0.45ml、由实施例 19 得到的高分子化催化剂 $1.136\mu\text{mol}$ （按 $\text{Al}/\text{M}=500$ ）、乙烯于 20°C 反应 0.5 小时，用含 1% 盐酸的乙醇溶液终止反应，将所得产物过滤，用乙醇洗涤 3 次，并于 40°C 真空干燥 24 小时，得聚乙烯 0.10 g，活性为 1.72×10^5 g PE/(mol Ni h)。

实施例 25：乙烯均相和非均相聚合

操作同实施例 22，甲基铝氧烷 2.0ml（按 $\text{Al}/\text{Ni}=4000$ ），得聚乙烯 0.183 g，活性为 3.22×10^5 g PE/(mol Ni h)。

实施例 26：乙烯均相和非均相聚合

操作同实施例 22, 于 50℃ 聚合, 得聚乙烯 0.255 g, 活性为 2.24×10^5 g PE/(mol Ni h)。

实施例 27: 乙烯均相和非均相聚合

操作同实施例 22, 于 50℃, 7 个大气压下聚合, 得聚乙烯 1.7g, 活性为 3.0×10^6 g PE/(mol Ni h)。

实施例 28: 乙烯均相和非均相聚合

操作同实施例 25, 乙烯压力为 20 个大气压, 于 12℃ 聚合, 得聚乙烯 7.31 g, 活性为 1.11×10^7 g PE/(mol Ni h)。